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| (54) Title: OPTICALLY CLEAR ANTISTATIC PRESSURE-SENSITIVE ADHESIVE FILM (57) Abstract An antistatic, removable pressure-sensitive adhesive film comprising a transparent flexible polymeric film support bearing on at least one major surface thereof a non-tribocharging, microparticulate blend adhesive formed from a blend of conductive, polymeric, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric microparticles, said microparticles having a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer, and at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, wherein said microparticles have an average diameter of at least 1 micrometer, and a nonparticulate acrylic copolymer; the adhesive having an adhesion to steel of from about 0.1 Newtons/100 mm (N/100 mm) to about 5 N/100 mm, and an optical transmission value of at least about 80 %. | | |

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OPTICALLY CLEAR ANTISTATIC PRESSURE-SENSITIVE ADHESIVE FILM**Background of the Invention****Field of the Invention**

The invention relates to optically clear antistatic microparticulate blend pressure-sensitive adhesive films useful in applications requiring elimination of electrostatic charge. These adhesive films provide excellent prevention of static charge build-up while having low adhesion and water-resistance.

Description of the Art

Electronic equipment, especially those instruments having smooth polymeric or glass surfaces, such as cathode ray tubes, liquid crystal display panels, computer screens and the like require protection during assembly, handling, shipping and the like. Typical protective elements prevent physical damage; such elements if attached exhibit tribocharge buildup which may damage the surface, or electronic components attached thereto.

Antistatic adhesives, when coated on selected substrates and suitably converted, provide antistatic, pressure-sensitive adhesive tapes or films. However, many of these products are difficult to cleanly remove from glass surfaces, have fillers, substrates or other ingredients which are opaque or hazy which is not pleasing aesthetically and which prohibits visual inspection of the surface while the protective film is in place. It would also be desirable to be able to apply the film in production and still be able to test the function, e.g., view the image on the screen of an electronic device, through the film thickness rather than removing and replacing such film for any unit which requires post production testing.

A number of conventional methods have been used for preparing antistatic adhesive compositions. One common method is the addition of conductive moieties to conventional adhesive formulations. Antistatic species may be introduced as conductive materials such as electrically conductive metal or carbon particles. Compositions of this type are disclosed in prior art references including EP 276691A, EP 0518722A, U.S. 4,606,962, EP 0422919A, U.S. 3,104,985, U.S. 4,749,612 and U.S. 4,548,862.

The addition of ionic materials to reduce generation of static charge is also known. Suitable materials of this type include ion conducting species such as those disclosed in Japanese patents JP 61,272,279 and JP 63,012,681.

U.S. 4,098,945 discloses a conductive composition which comprises a polymeric binder system, a plurality of insoluble spherical domains dispersed in the system, and at least one electrically conductive filler dispersed in the binder which provides conductive pathways through the composition. The spherical domains are preferably adhesive microspheres, the use of which lessens the amount of conductive filler used.

Yet another type of antistatic tape material is provided using a metal foil tape backing. One example of this, disclosed in U.S. 3,497,383, provides embossed foil tapes where contact points of metal project from the surface of the adhesive. However, this tape does not allow viewing of the surface through the tape.

No tapes available today provide all of the properties described above as optimal for good performance and appearance; those having low adhesion tend to have less effective antistatic properties, and those which provide good antistatic properties may have higher adhesion than desirable for clean removal, i.e., they may leave unsightly adhesive transfer on the surface. Further, they are not optically clear.

Surprisingly, the present invention provides an adhesive film which is optically clear for viewing and testing, will remain in place during shipping, and yet provides easy removability when desired. Further, the films of the invention provide exceptional antistatic properties, thus exhibiting significantly lower charges when the film is removed from the glass surface than any product currently available.

The unique properties of materials of the present invention are provided by the use of a blend of a nonparticulate acrylic copolymer and acrylic polymeric microparticles having attached polymer electrolyte complexes on the surface of each microparticle.

U.S. Patent 5,378,405 discloses an antistatic tape comprising conductive, polymeric, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric, acrylic pressure-sensitive adhesive microparticles having an average diameter of at least 1 micrometer, and having an ionic conductive material present on the surface which has been formed from a polymer electrolyte base polymer and an ionic salt.

Complexes of polyethylene oxide (PEO) and lithium salts have been shown to be promising materials as solid state polymer electrolytes. Lithium salts, like those disclosed in WO 8,303,322, U.S. 4,471,037 and FR 2,568,574, are most commonly used with PEO

in polymer electrolytes. Other metal salts such as alkaline earth salts may also enhance electrolytic properties as described in U.S. 5,162,174.

Particulate adhesives are known in the art, and have been coated on a variety of substrates and used primarily in applications requiring a low level of adhesion, e.g.,
5 removability. Such spheres and their use in aerosol adhesive systems having repositionable properties are disclosed in U.S. Pat. No. 3,691,140 (Silver). These microparticles are prepared by aqueous suspension polymerization of alkyl acrylate monomers and ionic comonomer, e.g., sodium methacrylate, in the presence of an emulsifier. The use of a water-soluble, substantially oil-insoluble ionic comonomer is critical to preventing
10 coagulation or agglomeration of the microparticles.

However, it has now been discovered that it is possible to provide a pressure-sensitive adhesive film or tape format made from a blend including microparticulate adhesives, and certain nonparticulate acrylic copolymers which are extremely effective in dissipating electrostatic charge, allow visual inspection and testing through the antistatic
15 film, are extremely water-resistant, and cleanly removable from glass or transparent polymeric surfaces.

Summary of the Invention

The invention provides an antistatic, removable pressure-sensitive adhesive film comprising a transparent flexible polymeric film support bearing on at least one major
20 surface thereof a non-tribocharging, microparticulate blend adhesive formed from a blend of a nonparticulate acrylic copolymer and conductive, polymeric, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric microparticles. The tape has good optical clarity, and is especially useful for protecting glass panels such as computer screens, liquid crystal display (LCD) panels and the like during shipment, while providing easy removal.
25 The film does not exhibit tribocharging either while in place or when removed. The film also has resistance to high humidity and water.

Useful microparticulate blend pressure-sensitive adhesive compositions comprise a blend of

- a) 100 parts acrylate or modified acrylate particles having a surface comprised
30 of chains of an ionically conducting polymer electrolyte, preferably polyethylene oxide, and

- b) from 1 to 50 parts of a nonparticulate acrylic copolymer.

The microparticles useful herein may be solid microparticles or hollow ones, as desired.

Where hollow microparticles are desired, one or more voids may be present

More specifically, the invention provides an optically clear, water-resistant, anti-static removable pressure-sensitive adhesive film comprising a transparent flexible substrate having opposing surfaces, at least one surface bearing thereon an optically clear pressure-sensitive adhesive comprising a blend of:

- 1) 100 parts conductive, polymeric, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric, acrylic microparticles comprising 100 parts monomers, comprising:
- a) from 70 to 99 of at least one monomer selected from alkyl (meth)acrylate esters and vinyl esters; and
- b) up to 15 parts by weight of at least one polar monomer,
- c) from 0.1 part to 10 part of a polymer electrolyte,
- d) at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals,
- said adhesive having an adhesion to steel of from 0.1 N/100 mm to 5 N/100 mm;
- 2) from 1 to 50 parts of a nonparticulate acrylic copolymer, and
- 3) from 0 to 1.5% of an aziridine crosslinker.

In another embodiment herein, the microspheres are blended with another particulate; i.e., nontacky acrylic microspheres. Preferred particulate mixtures can be described as follows:

An optically clear, antistatic, removable pressure-sensitive adhesive film comprising a transparent flexible polymeric film support bearing on at least one major surface thereof a non-tribocharging, microparticulate blend adhesive formed from a blend of:

- a) conductive, polymeric, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric microparticles, said microparticles having a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer, and at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, wherein said microparticles have an average diameter of at least 1 micrometer, and

- b) conductive, polymeric, nontacky, solvent-insoluble, solvent-dispersible, elastomeric microparticles,

said adhesive having an adhesion to steel of from 0.1 Newton/100 mm (N/100 mm) to 5 N/100 mm, and an optical transmission value of at least 80%.

5 As used herein, these terms have the following meanings.

1. The term "polymer electrolyte" means a polymeric species containing electron donating atoms which may be associated with acceptor atoms.

2. The term "polymer electrolyte base polymer" means a polymer which is capable of forming a polymer electrolyte during formation of the microparticle.

10 3. The term "polymer electrolyte functional unit" means the group containing the electron donating species.

4. The term "microparticle" means a particle having a diameter of from about 1 micrometer to about 250 micrometers.

15 5. The term "tribocharging" means electrostatic charge generation associated with friction between separable surfaces.

6. The term "droplet" means the liquid stage of the microparticles prior to the completion of polymerization.

7. The term "cavity" means a space within the walls of a droplet or microparticle when still in the suspension or dispersion medium prior to drying, and thus
20 containing whatever medium was used.

8. The term "void" means an empty space completely within the walls of a polymerized microparticle.

9. The term "hollow" means containing at least one void or cavity.

10. The term "solid" means voids or cavity-free.

25 11. The term "alkyl (meth)acrylate" means an alkyl acrylate or alkyl methacrylate.

12. The term "modified surface" means a surface which has been subjected to a priming, coating or treatment such as chemical or radiation treatment such that the original properties of the surface have been changed.

30 13. The term "optically clear" means an adhesive film having an optical transmission value of at least about 80%, when tested as described herein.

14. The term "optical transmission value" means the percentage of light that is not either reflected back toward the source or absorbed by the film as a percentage of the total incident light at a wavelength of 550 nm. (light emitted/light source x 100).

As used herein, all parts, percents, and ratios are by weight, unless specifically
5 stated otherwise.

Detailed Description of the Invention

Films, or tapes of the invention are suitable for use in a variety of applications where transport of electrical current or prevention of electrostatic charge is important. However, films of the invention are especially useful in that portion of the industry in
10 which products have viewing of images through a glass or plastic "screen". This includes devices receiving images from computers or signals from remote locations, e.g., televisions, computer screens, LCD panels, and the like, as well as screens which are merely viewing glass for images or displays immediately beneath the glass, e.g., glass placed over LED readouts. Such smooth surfaces require physical protection from
15 scratching during handling and shipment, as well as electronic protection from tribocharging which could damage the electronics within. To be useful, a protective adhesive film must have an adhesion sufficiently low that they can be removed when desired. The films do not exhibit any adhesive buildup or tribocharging occurring on the image transmission surface. The removal is typically achieved by peeling the adhesive film
20 from the surface, and both the adhesive and the film substrate therefor must be flexible in order to remove cleanly, and the adhesion to the film substrate must be higher than the adhesion to the bonded surface.

Useful microparticulate blend adhesives have adhesion values to steel of from 0.1 N/100 mm to 5 N/100 mm, preferably from 0.1 N/100 mm to 2 N/100 mm.

25 Such films should also be transparent, i.e., have an optical transmission value of at least 80%, for testing and inspection purposes as well as aesthetic effects. Preferred films of the invention have optical transmission values of at least 85%; most preferably at least 90%.

Useful microparticles comprise alkyl acrylate or methacrylate monomers, especially
30 monofunctional unsaturated acrylate or methacrylic esters of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to 14 carbon atoms. Such acrylates are oleophilic,

water emulsifiable, have limited water solubility, and as homopolymers, generally have glass transition temperatures below about -20°C . Included within this class of monomers are, for example, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl
5 methacrylate, isononyl acrylate, isobornyl acrylate, isodecyl acrylate, and the like, singly or in mixtures.

Preferred acrylates include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate, and mixtures thereof. Acrylate or methacrylate or other vinyl monomers which, as homopolymers, have
10 glass transition temperatures higher than about -20°C , e.g., butylmethacrylate, methyl methacrylate, ethyl acrylate, tert-butyl acrylate, vinyl acetate, and the like, may be utilized in conjunction with one or more of the acrylate or methacrylate monomers provided that the glass transition temperature of the resultant polymer is below about -20°C .

15 Useful vinyl ester monomers are those which form homopolymers having glass transition temperatures below about 10°C . Such esters comprise 1 to 14 carbon atoms, and includes such monomers as vinyl 2-ethylhexanoate, vinyl caprate, vinyl laurate, vinyl pelargonate, vinyl hexanoate, vinyl propionate, vinyl decanoate, vinyl octanoate, and the like.

20 Useful polar monomers include N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl acrylate, and diallyl phthalate, acrylic acid, methacrylic acid, itaconic acid, hydroxyalkyl acrylates, cyanoalkyl acrylates, acrylamides, substituted acrylamides. When more than one polar monomer is used, mixtures may include monomers having similar or unlike polarities, e.g., one moderately polar and one strongly polar monomer or
25 two monomers from one group.

The conductive microparticles and the pressure-sensitive adhesives made therefrom comprise at least 70 parts by weight of at least one alkyl (meth)acrylate ester or vinyl ester and correspondingly, up to 30 parts by weight of one or more polar monomers.

Highly preferred microparticles comprise two alkyl (meth)acrylate monomers,
30 which seem to yield optically clear adhesives, without haze, i.e., combinations of isooctyl acrylate, and 2-ethyl hexyl acrylate.

Polymer electrolyte base polymers suitable for use in the invention include polyethylene oxide, polyphenylene oxide, polyphenylene sulfide, polyethylene sulfide, polyethyleneimine, polypropylene oxide, polybutylene oxide, polybutylene sulfide, polybutylene imine, and the like. Polyethylene oxide is preferred. Useful amounts of the polymer electrolyte base polymer in microparticles of the invention range from 0.1 part to 10 parts, preferably from 1 part to 5 parts, based on 100 parts monomer weight.

Further crosslinking agents may also be included, such as a multifunctional (meth)acrylate, e.g., butanediol diacrylate or hexanediol diacrylate, or other multifunctional crosslinker such as divinylbenzene. When used, the crosslinker(s) is(are) added at a level of up to 1 percent, preferably up to 0.5 percent, of the total polymerizable composition.

The conductive properties of the polymeric microparticles are further enhanced by the addition of ionic salts to adhesive compositions which contain the microparticles. It is believed that the ionic salts become associated with the electron donating groups present in the amorphous polymer domains. The adhesive contains from 0.01 mole to 10 moles of at least one salt of an alkali metal or alkaline earth metal per mole of polymer electrolyte base unit; preferably from 0.5 mole to 5 mole, most preferably from 0.1 mole to 1 mole.

Salts used for this purpose include salts of alkali metals, and alkaline earth metals, including but not limited to, NaI, NaSCN, BaCF₃SO₃, NaBr, NaClO₄, LiCl, LiNO₃, LiCF₃SO₃, LiSO₄, LiOH and KOH. Lithium salts are preferred for the present invention, especially lithium nitrate.

Microparticulate blend adhesives of the invention also comprise at least one nonparticulate acrylic copolymer. The blends comprise from 1 to 50 parts of nonparticulate copolymer per 100 parts of microparticles. Commercially available examples include Rhoplex® resins, available from Rohm and Haas, including Rhoplex®-R AC-630, and Rhoplex® R-225.

Where high water-resistance is critical, the composition may also contain an aziridine crosslinking agent. Useful aziridines include pentaerythritol-tris-(β-(N-aziridinyl)propionate) and trimethylolpropane-tris-(β-(N-aziridinyl)propionate), both available under the trade name "XAMA", i.e., XAMA-2 and XAMA-7, from B.F.

Goodrich Specialty Chemicals. Surprisingly, the use of such aziridines provides the water-

resistance necessary while maintaining the required balance of adhesion, antistatic properties and removability. When used, the aziridine is present in an amount of from 0.5% to 1.5%.

In another embodiment, the optically clear film of the invention comprises a combination of tacky acrylic microspheres and nontacky acrylic microspheres. These may be used in ratios of from 1/99 tacky to nontacky to 80/20, depending on the identity of the monomers used and the adhesion strength of the tacky microspheres. Preferred ratios are from 5/95 to 30/70, most preferably up to 15/85. Useful nontacky or "tack free" microspheres include those disclosed in WO 93/12147, which comprise alkyl (meth)acrylates, polar monomers and a multifunctional crosslinking agent. The nontacky microspheres are made by suspension polymerizations similar to those described for the tacky microspheres herein.

Films of the present invention display dramatically different tribocharging properties than continuous adhesive layers of similar chemical components. For example, when coated on a film substrate, an acrylate-based emulsion adhesive produces a continuous film with a planar surface. Upon application and removal from a planar surface, this adhesive film will cause generation of charged species on the surface of the adhesive and on the planar surface to which it was attached. The residual charge has a magnitude of up to several thousand volts. However, adhesive film samples of the current invention, under similar conditions generate almost no charge upon removal from the planar surface.

Electrical characteristics of pressure-sensitive adhesives of the invention vary from somewhat resistive to significantly conductive materials.

The microparticles and emulsion containing the microparticles may be prepared by various emulsification processes, which are varied depending on whether hollow or solid microparticles are desired. Aqueous suspensions of hollow microparticles may be prepared by a "two-step" emulsification process which first involves forming a water-in-oil emulsion of an aqueous solution of polar monomer(s) in oil phase monomer, i.e., at least one (meth)acrylate or vinyl ester monomer, with a polymer electrolyte base polymer, using an emulsifier having a low hydrophilic-lipophilic balance (HLB) value. Suitable emulsifiers are those having an HLB value below about 7, preferably in the range of about 2 to about

7. Examples of such emulsifiers include sorbitan monooleate, sorbitan trioleate, and ethoxylated oleyl alcohol such as Brij™ 93, available from Atlas Chemical Industries, Inc.

Thus, in this first step, oil phase monomer(s), polymer electrolyte base polymer, emulsifier, a free radical initiator, and a crosslinking monomer or monomers are combined, and an aqueous solution of all or a portion of the polar monomer(s) is agitated and poured into the oil phase mixture to form a water-in-oil emulsion. The polymer electrolyte base polymer may be added to either the oil phase or the water phase. A thickening agent, e.g., methyl cellulose may also be included in the aqueous phase of the water-in-oil emulsion. In the second step, a water-in-oil-in-water emulsion is formed by dispersing the water-in-oil emulsion of the first step into an aqueous phase containing an emulsifier having an HLB value above about 6. The aqueous phase may also contain any portion of the polar monomer(s) which was not added in step one. Examples of such emulsifiers include ethoxylated sorbitan monooleate, ethoxylated lauryl alcohol, and alkyl sulfates. In both steps, when an emulsifier is utilized, its concentration should be greater than its critical micelle concentration, which is herein defined as the minimum concentration of emulsifier necessary for the formation of micelles, i.e., submicroscopic aggregations of emulsifier molecules. Critical micelle concentration is slightly different for each emulsifier, usable concentrations ranging from about 1.0×10^{-4} to about 3.0 moles/liter. Additional detail concerning the preparation of water-in-oil-in-water emulsions, i.e., multiple emulsions, may be found in various literature references, e.g., Surfactant Systems: Their Chemistry, Pharmacy, & Biology, (D. Attwood and A. T. Florence, Chapman & Hall Limited, New York, New York, 1983).

The final process step of this method involves the application of heat or radiation to initiate polymerization of the monomers. Useful initiators are those which are normally suitable for free radical polymerization of acrylate or vinyl ester monomers and which are oil-soluble and of very low solubility in water.

Examples of such initiators include azo compounds, hydroperoxides, peroxides, and the like, and photoinitiators such as benzophenone, benzoin ethyl ether, and 2,2-dimethoxy-2-phenyl acetophenone.

Use of a water-soluble polymerization initiator causes formation of substantial amounts of latex. The extremely small particle size of latex particles renders any

significant formation of latex undesirable. The initiator is generally used in an amount ranging from 0.01 percent up to 10 percent by weight of the total polymerizable composition, preferably up to 5 percent.

Aqueous suspensions of hollow conductive microparticles may also be prepared by a "one-step" emulsification process comprising aqueous suspension polymerization of at least one alkyl (meth)acrylate ester monomer or vinyl ester monomer and at least one polar monomer and a polymer electrolyte base polymer in the presence of at least one emulsifier capable of producing a water-in-oil emulsion inside the droplets which is substantially stable during emulsification and polymerization. As in the two-step emulsification process, the emulsifier is utilized in concentrations greater than its critical micelle concentration. In general, high HLB emulsifiers are required, i.e., emulsifiers having an HLB value of at least 25, will produce stable cavity-containing droplets during the polymerization, and are suitable for use in this one-step process. Examples of such emulsifiers include alkylarylether sulfates such as sodium alkylarylether sulfate, e.g., Triton™ W/30, available from Rohm and Haas, alkylaryl polyether sulfates such as alkylaryl poly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy repeat units, and alkyl sulfates such as sodium lauryl sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate, and sodium hexadecyl sulfate, alkyl ether sulfates such as ammonium lauryl ether sulfate, and alkyl polyether sulfates such as alkyl poly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy units. Alkyl sulfates, alkyl ether sulfates, alkylarylether sulfates and mixtures thereof are preferred as they provide a maximum void volume per microparticle for a minimum amount of surfactant. Nonionic emulsifiers, e.g., Siponic™ Y-500-70 (ethoxylated oleyl alcohol), commercially available from Alcolac, Inc., and Pluronic™ P103 (a block copolymer of polypropylene oxide and polyethylene oxide) commercially from BASF Corporation) can be utilized alone or in conjunction with anionic emulsifiers. Polymeric stabilizers may also be present but are not necessary.

Solid microparticles useful in adhesive films of the invention may be made by a similar one-step process comprising aqueous suspension polymerization of at least one alkyl (meth)acrylate ester monomer or vinyl ester monomer, at least one polar monomer and a polymer electrolyte base polymer in the presence of a suspension stabilizer. It is not necessary to use a high HLB emulsifier because the droplets formed need not be cavity-

containing droplets. Examples of useful lower HLB emulsifiers include ammonium lauryl sulfate such as Standapol™ A, available from Hercules and other steric or electrosteric polymeric stabilizers such as (poly)vinyl alcohol, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl pyrrolidone, polyvinyl methylether, and the like.

- 5 Preparation of microparticles may be modified by withholding the addition of all or part of the polymer electrolyte base polymer, and polar monomers until after polymerization of the oil phase is initiated; however, the components must be added to the polymerizing mixture prior to 100% polymer conversion.

- Discrete conductive polymeric microparticles may also be prepared via suspension
10 polymerizations disclosed in U.S. Pat. No. 3,691,140, US 4,166,152, US 4,636,432, US 4,656,218, and US 5,045,569, for preparing adhesive compositions.

- The conductive microparticles are normally tacky, elastomeric, insoluble but swellable in organic solvents, and small, typically having diameters of at least 1 micrometer, preferably in the range of 1 to 250 micrometers, more preferably from 1 to 50
15 micrometers. They may be solid or contain a single void, or multiple voids.

- Following polymerization, an aqueous suspension of the microparticles is obtained which is stable to agglomeration or coagulation under room temperature conditions. The suspension may have non-volatile solids contents of from 10 to about 50 percent by weight. Where high HLB emulsifiers are used the droplets have one or more cavities
20 which, upon drying, become voids. Both phases may contain a minor portion of small latex particles.

The microparticles are subsequently physically blended with the nonparticulate acrylic copolymer, the crosslinking agents, ionic material, and other adjuvants.

- Adhesives of the invention may also comprise other adjuvants, when used in minor
25 amounts so as not to affect the clarity of the adhesive.

- Films of the invention may be produced by coating the blend adhesive compositions of the invention onto a flexible substrate which will allow sufficient flex to peel off a large geometric piece of film without causing delamination of the adhesive or tearing of the backing. Suitable substrates include polymeric films such as vinyl,
30 polyesters, especially polyethylene terephthalate, poly-phenylene sulfide, polyethylene, polypropylene, (nonoriented or biaxially oriented, known as BOPP), and the like.

The coating may be carried out by conventional methods such as knife coating, Meyer bar coating, knurled roll, and other conventional means known in the art for coating adhesives such as use of an extrusion die. The adhesive may be coated to a thickness of from 10 μm to 125 μm .

5 Primer or binders may be used, but they are not required. Preferred embodiments comprise a binder to ensure that the adhesion between the backing and the adhesive exceeds the adhesion between the adhesive and the transparent surface to which it will be attached. Useful primers include phenolic resins, and the like, e.g., a phenol formaldehyde resin.

10 Where high-temperature properties are required, a useful primer will comprise at least one phenolic resin and at least one rubbery component. Useful rubbery components include natural rubbers such as butyl rubbers, and various synthetic compounds, including but not limited to, acrylonitrile-butadiene, acrylonitrile-butadiene-styrene copolymers, styrene-butadiene-styrene, styrene-ethylene butylene-styrene, polychloroprene,
15 polybutadiene, polyisoprene, styrene-isoprene-styrene, and mixtures thereof. Preferred primers contain mixtures of two or more rubbery compounds, such as acrylonitrile-butadiene, and polychloroprene.

Useful phenolic resins, include but are not limited to, phenol formaldehyde resin, available commercially from Union Carbide under the trade names UCAR BKR-2620, and
20 UCAR CK-1635, novolak resins and the like, and mixtures thereof. Such primers contain from 40 to 120, preferably from 40 to 100 parts of phenolic resin per 100 parts of rubbery compound.

When used, a primer may further comprise additives such as tackifying agents, antioxidants, colorants, viscosity adjusting agents, solvents and other conventional
25 additives, which may be used in such amounts as are known in the art, but such additives are preferably present only in small amounts, so as not to increase the haze of the adhesive film.

The film may be commercialized in roll form, or may be divided into segments for sale, such as die-cut geometric shapes. Additionally, the adhesive may be provided
30 between two substrates, e.g., the adhesive is coated onto a film substrate which may be provided on a low adhesion backsize or other easily removable surface for individual use.

The adhesion properties of the adhesives may be altered by addition of tackifying resin and/or plasticizer. Preferred tackifiers for use herein include hydrogenated rosin esters commercially available from companies such as Hercules Inc., under such trade names as Foral™ 65, Foral™ 85, and Foral™ 105. Other useful tackifiers include those
5 based on t-butyl styrene. Useful plasticizers include dioctyl phthalate, 2-ethyl hexyl phosphate, tricresyl phosphate, and the like.

These and other aspects of the invention are illustrated by the following examples which should not be viewed as limiting in scope.

Test Methods

10 Resistivity Measurements of Antistatic Coatings

Resistivity is a measure of the intrinsic ability of a material to conduct electrons. It is a property which is independent of the dimensions of the material sample.

The surface resistivity of coatings of the invention was measured by connecting a Keithley 616 digital electrometer (Keithley 6105 resistivity adapter) to a 500 volt power
15 supply, and attaching to an electrometer. Individual samples were measured using standard procedures according to ASTM D-257.

Peel Adhesion

Peel adhesion is the force required to remove a coated flexible sheet material from a test panel measured at a specific angle and rate of removal. In the examples, this force is
20 expressed in Newtons per 100 millimeters width of coated sheet. The procedure followed is:

A strip 1.27 cm in width of the coated sheet is applied to the horizontal surface of a clean glass test plate with at least 12.7 lineal cm in firm contact. A 2 kg hard rubber roller is used to apply the strip. The free end of the coated strip is doubled back nearly touching
25 itself so the angle of removal will be 180°. The free end is attached to the adhesion tester scale. The steel test plate is clamped in the jaws of a tensile testing machine which is capable of moving the plate away from the scale at a constant rate of 2.3 meters per minute. The scale reading is recorded as the film is peeled from the steel surface. The data is reported as the average of the range of numbers observed during the test.

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Glossary

| | | |
|----|---------------------|--|
| | IOA | Isooctyl Acrylate |
| | AA | Acrylic Acid |
| | PEO ₉ MA | Polyethylene Oxide Methacrylate |
| 5 | BPER | 70% Benzoyl Peroxide, Lucidol™ 70 |
| | ALS | Ammonium Lauryl Sulfate, |
| | Standapol™ A | Ammonium Lauryl Sulfate from Hercules |
| | Lithium Nitrate | 20% solution in distilled water. |
| | Benzotriazole | Anti-corrosion agent, as a 10% solution in 50/50 |
| 10 | | iPrOH/Water |
| | XAMA-7 | Pentaerythritol-tris-(β-(N-aziridiny)propionate) crosslinker |
| | XAMA-2 | Trimethylolpropane-tris-(β-(N-aziridiny)propionate) crosslinker |

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ExamplesPreparation of IOA/AA/PEO₉MA Microparticles

Acrylic acid (4.8 g), polyethylene oxide methacrylate (PEO₉MA)(95/2/3) (7.2 g), and 75% benzoyl peroxide (1.05 g) were dissolved in isooctyl acrylate (232.8 g). This solution was added to an aqueous solution of surfactant. The surfactant solution

20 comprised Standapol™ A, available from Hercules, (4 g) dissolved in de-ionized water (360 g). An emulsion of the isooctyl acrylate solution in the aqueous solution was produced by high shear mixing using an Omni mixer at setting 5. Mixing was continued until the average particle size of the oily droplets was approximately 3 μm. Size was determined using an optical microscope.

25 The resulting oil-in-water emulsion was charged to a 1-liter resin reactor equipped with four baffles, a paddle stirrer and a suitable heat source, such as a heating mantle. With continuous stirring at a rate of 400 rpm, the reactor and contents were heated to 60°C.

30 At this point the reactor was degassed with nitrogen. A reaction proceeded in the absence of oxygen. This was allowed to continue for a period of 5 hours while both

temperature and stirring rate were maintained. The resulting aqueous suspension contained insoluble particles of approximately 5 μm in diameter.

Preparation of IOA/EA/PEO₉MA Microparticles 75/20/2/3

Acrylic acid (4.8 g), ethyl acrylate (48 g), polyethylene oxide methacrylate (72 g) and 75% benzoyl peroxide (1.05 g) were dissolved in isooctyl acrylate (180 g). This solution was added to an aqueous solution of surfactant. The surfactant solution comprised Standapol®A, available from Hercules, (4 g) dissolved in de-ionized water (360 g) in a glass-lined vessel. An emulsion of the isooctyl acrylate solution in the aqueous solution was produced by high shear mixing using a Gifford-Wood mixer; mixing continued until the average particle size of the oily droplets was approximately 5 μm . Size was determined using an optical microscope.

The resulting oil-in-water emulsion was charged to a 1-liter glass resin reactor equipped with four baffles, a paddle stirrer and a suitable heat source, such as a heating mantle. With continuous stirring at a rate of 400 rpm, the reactor and contents were heated to 65°C.

At this point the reactor was degassed with nitrogen. A reaction proceeded in the absence of oxygen. This was allowed to continue for a period of 5 hours while both temperature and stirring rate were maintained. The resulting aqueous suspension contained insoluble particles of approximately 5 μm in diameter.

To 100 parts of this particulate adhesive, was added a combination of lithium salts to increase ionic conductivity, ammonium hydroxide for pH adjustment, benzotriazole for corrosion inhibition and a crosslinker to improve water resistance of the coating. Each of the additional ingredients was slowly stirred into the adhesive composition and thoroughly mixed just prior to coating.

Preparation of IOA/EA/HDDA/PEO₉MA Non-Tacky Microparticles

Ethyl acrylate (64.0 g), polyethylene oxide methacrylate (9.6 g), 1,6 hexanedioldiacrylate (6.4 g) and isooctylacrylate were combined to provide a monomer solution. Addition of Vazo 52 initiator (azobisvaleronitrile - 1.06 g) yielded a solution that dispersed effectively in a surfactant containing aqueous phase. The aqueous phase comprised Standapol-A (5.12 g) dissolved in de-ionized water (480 g). With high shear

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mixing, e.g. using an Omni mixer at setting 5, the droplets of initiator-containing monomer solution decreased in size to provide an emulsion having dispersed droplets of approximately 1 μm . Size may be determined using an optical microscope.

The resulting oil-in-water emulsion was charged to a 1-liter resin reactor equipped with four baffles, a paddle stirrer and a suitable heat source, such as a heating mantle. With continuous stirring at a rate of 400 rpm, the reactor and contents were heated to 50°C.

At this point the reactor was degassed with argon. A reaction proceeded in the absence of oxygen. This was allowed to continue for a period of 3 hours while both temperature and stirring rate were maintained. The resulting aqueous suspension contained insoluble particles of 2-3 μm in diameter.

Example 1

The above microspheres were stirred together in water with the other ingredients, stirring between each addition. The adhesive was filtered and coated onto 25 μm P114 primed polyester film, using a flat bed notched bar coater with the orifice set at 125 μm . The coated film was then dried in a forced air oven at 104°C for 10 minutes, allowed to equilibrate in a constant temperature/constant humidity room for 24 hours, and then tested for adhesion. The adhesion of the sample was 1.08N/100 mm (28 g/in). The film had an optical transmission value of 82.5%.

| FORMULA | |
|---|---------|
| IOA/AA/M90G (95/2/3) @ 40% in water | 100.0 g |
| Rhoplex® AC 630 Acrylic Emulsion Polymer @ 50% in water | 20.0 g |
| Ammonium Hydroxide dropwise until neutral by pH paper | |
| Lithium Nitrate @ 20% in water | 3.0 g |
| UCAR Polyphobe 104 Thickener @ 25% in water | 0.5 g |

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Example 2

The above described microparticles were mixed together in the order listed below, with stirring between each addition. The adhesive was filtered and coated onto 25 μ m P114 primed polyester film, using a flat bed notched bar coater with the orifice set at 100 μ m. The coated film was then dried in a forced air oven at 104°C for 10 minutes, allowed to equilibrate in a constant temperature/constant humidity room for 24 hours, and then tested for adhesion. The adhesion of the sample was 0.462N/100 mm (12 g/in). The film had an optical transmission value of 90.1%.

| FORMULA | |
|--|---------|
| IOA/EA/AA/M90G (75/20/2/3) @ 40% in water | 100.0 g |
| Rhoplex® R-225 Acrylic Emulsion Polymer @ 38% in water | 7.2 g |
| Benzotriazole @ 10% in 50/50 IPA/water | 0.5 |
| Lithium Nitrate @ 20% in water | 3.0 g |
| XAMA-7® @ 10% in IPA | 0.9 g |

10

Example 3

The above described microparticles were mixed together in the order listed below, with stirring between each addition. The adhesive was filtered and coated onto 25 μ m primed BOPP films using a #19 Meyer rod, followed by blow drying for several minutes at 60°C until the film became clear. The adhesion was 1.6 N/100 mm. The higher value compared to the adhesion for the previous examples, reflects the use of BOPP. The film had an optical transmission value of 87.7%.

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| FORMULA | |
|---|---------|
| IOA/EA/AA/M90G adhesive 75/20/2/3 | 100.0 g |
| 20% Lithium Nitrate solution | 3.0 g |
| 10% Benzotriazole in 50/50 iPrOH-Water | 0.5 g |
| 10% XAMA-7® Aziridine crosslinker in iPrOH | 0.7 g |
| 8% Lithium Hydroxide solution | 1.0 g |
| Rhoplex® R-225 (Rohm and Haas) Acrylic emulsion | 10.0 g |

| Comparative Electrical Properties | | | | |
|---|----------------------|---|-------|-------------------|
| Film | Resistivity | Volts Residual Charge | | |
| | | (2 x 5" sample removal from 3M 711 tester 55% RH) | | |
| | (Ohm/Sq 55% RH) | Steel Plate | Glass | Polarization Film |
| Invention | 7.6×10^8 | 3 | 6 | 12 |
| Korea Antistatic Panel Film | 9.2×10^{10} | 1176 | 1676 | 1330 |
| Polarization Protective Film Arisawa Mfg | $>1 \times 10^{14}$ | >2000 | >2000 | >2000 |

Example 4

- 5 240 g of IOA, 64 g of ethyl acrylate, 9.6 g of M90G and 6.4 g of 1,6 hexanedioldiacrylate were mixed together. 1.06g of Vazo® 52 (azobisvaleronitrile) was dissolved in the monomers. 5.12 g of Standapol-A® was then dissolved in 480 g of DI H₂O. The monomer phase was mixed into the aqueous surfactant solution above and homogenized until the droplet size was approximately 1 micron. This emulsion was then
- 10 charged to a 1 liter reactor and heated to 50°C with mild agitation. At 50°C, the emulsion was then degassed with Ar and allowed to react for 3 hours.

Example 5Blending of Tacky and Non-Tacky Microparticles

The following table shows the varying amounts of non-tacky microparticles added to antistatic adhesive microparticles using dispersion for each that were adjusted to 40% solids in an aqueous dispersion phase.

The antistatic adhesive microparticulate dispersion comprised 95/2/3 IOA/EA/M90G at 40% solids in water. The non-tacky microparticulate dispersion comprised 75/20/3/2 IOA/3A/M90G/1,6,HDDA at 40% solids in water.

To 50 g of a selected blend were added 1.5 g of a 20% aqueous solution of LiNO_3 and 0.25 g of Polyphobe 104 (Union Carbide). The pH of the blend was adjusted to 8 using ammonium hydroxide.

Each coating formulation was coated at 100 μm (4 mils) wet onto 25 μm (1 mil) polyethyleneterephthalate. Coated films were dried at 65°C. Thereafter properties of adhesion, conductivity and tack were measured.

| % Non-Tacky Particulate | Adhesion to Glass (N/100 mm) | Probe Tack (gms) | Resistivity Ohms/sq. |
|-------------------------|------------------------------|------------------|----------------------|
| 0 | 4.4 | 181 | 6×10^6 |
| 10 | 4.9 | 214 | 5×10^6 |
| 20 | 2.2 | 265 | 5.3×10^6 |
| 40 | 0.8 | 309 | 5.9×10^6 |
| 60 | 0.40 | 278 | 5.6×10^6 |
| 90 | 0.16 | 79 | 8×10^6 |

What is Claimed is:

1. An optically clear, antistatic, removable pressure-sensitive adhesive film comprising a transparent flexible polymeric film support bearing on at least one major surface thereof a non-tribocharging, microparticulate blend adhesive formed from a blend
5 of:
 - a) conductive, polymeric, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric microparticles, said microparticles having a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer, and at least one ionic conductive material selected from the group
10 consisting of salts of alkali metals and salts of alkaline earth metals, wherein said microparticles have an average diameter of at least 1 micrometer, and
 - b) a nonparticulate acrylic copolymer,said film having an adhesion to steel of from 0.1 Newtons/100 mm (N/100 mm) to 5 N/100 mm, and an optical transmission value of at least 80%.
- 15 2. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 1 further comprising an aziridine crosslinking agent.
3. An optically clear, anti-static particulate pressure-sensitive adhesive according to claim 1, said adhesive having an adhesion of from 0.1 N/100 mm to 2 N/100 mm.
- 20 4. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 2, wherein said aziridine crosslinking agent is selected from the group consisting of pentaerythritol-tris-(β -(N-aziridiny)propionate) and trimethylolpropane-tris-(β -(N-aziridiny)propionate).
5. An optically clear, antistatic, removable pressure-sensitive adhesive film
25 according to claim 1 wherein said microparticulate blend adhesive comprises a polymer of monomers comprising:
 - a) at least 70 parts of at least one alkyl (meth)acrylate or vinyl ester,

b) correspondingly, up to 30 parts of at least one polar monomer, to make 100 parts monomer,

and wherein said ionic conductive material comprises a polymer electrolyte formed from a polymer electrolyte base polymer, said polymer electrolyte base polymer added in an amount of from 0.1 part to 10 parts, and from 0.01 moles to 10 moles of at least one salt of an alkali metal or alkaline earth metal per mole of polymer electrolyte base unit.

6. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 1 wherein said ionic conductive material is formed from a polymer electrolyte base polymer selected from the group consisting of polyethylene oxide, polyphenylene oxide, polyphenylene sulfide, polyethylene sulfide, polyethyleneimine, polypropylene oxide, polybutylene oxide, polybutylene sulfide, and polybutylene imine.

7. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 6 wherein the polymer electrolyte base polymer is polyethylene oxide and said ionic conductive material is selected from the group consisting of LiCl, LiNO₃, LiCF₃SO₃, LiSO₄, LiOH, KOH, NaSCN, NaI, BaSO₃CF₃, and NH₄OH.

8. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 5 wherein the alkyl (meth)acrylate is selected from the group consisting of isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isononyl (meth)acrylate, isoamyl (meth)acrylate, isodecyl (meth)acrylate, and butyl (meth)acrylate.

9. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 5 wherein the vinyl ester is selected from the group consisting of vinyl 2-ethylhexanoate, vinyl caproate, vinyl laurate, vinyl pelargonate, vinyl hexanoate, vinyl propionate, vinyl decanoate, and vinyl octanoate.

10. An optically clear, antistatic, removable pressure-sensitive adhesive film according to claim 5 wherein said polar monomer is selected from the group consisting of N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl acrylate, diallyl phthalate, acrylic acid, methacrylic acid, itaconic acid, hydroxyalkyl acrylates, cyanoalkyl acrylates, acrylamides, and substituted acrylamides.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/US 96/07669

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09J7/02 C09J133/08 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09J H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | WO,A,95 04356 (MINNESOTA MINING & MFG) 9 February 1995 see claims 1,9-12 | 1 |
| E | WO,A,96 20983 (MINNESOTA MINING & MFG) 11 July 1996 see page 18, line 10 | 1 |

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

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- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter nal Application No

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